

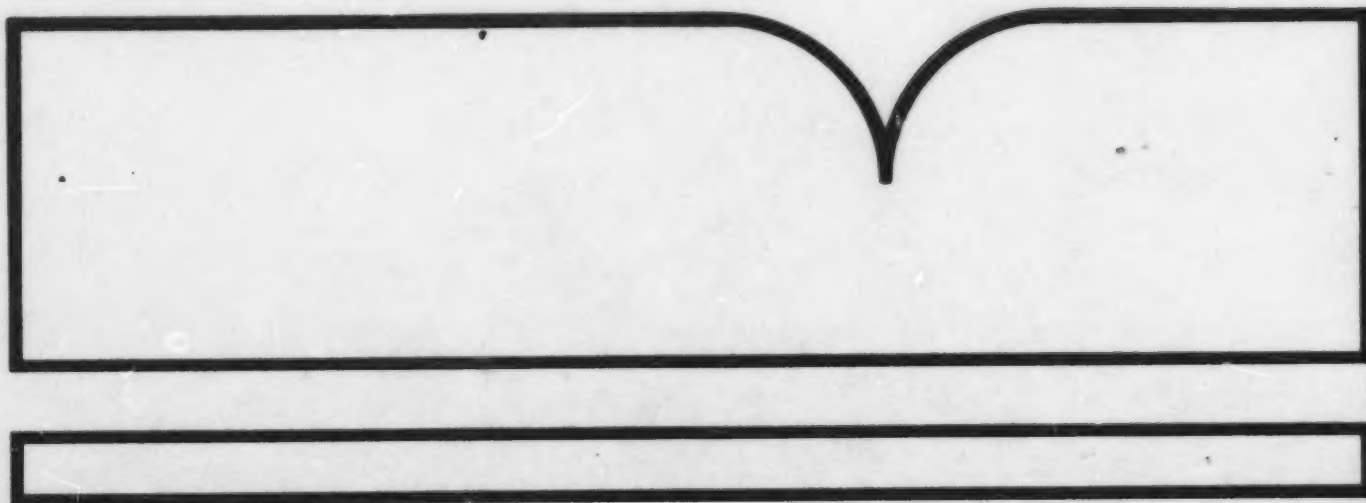
Formation and Transport of Ozone and
Aerosols in Power Plant Flumes

Washington Univ.
St. Louis, MO

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

1980



U.S. Department of Commerce
National Technical Information Service

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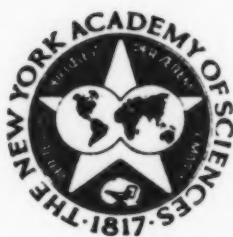
TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
1. REPORT NO. EPA-600/J-80-227	2. Journal Article	3. RECIPIENT'S ACCESSION NO. PB81 16662 1
4. TITLE AND SUBTITLE FORMATION AND TRANSPORT OF OZONE AND AEROSOLS IN POWER PLANT PLUMES	5. REPORT DATE	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Noor V. Gillani and William E. Wilson	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Washington University St. Louis, MO 63130	10. PROGRAM ELEMENT NO. C05A1A/16 - 0205 (FY-80)	
	11. CONTRACT/GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711	13. TYPE OF REPORT AND PERIOD COVERED	
	14. SPONSORING AGENCY CODE EPA/600/09	
15. SUPPLEMENTARY NOTES REFERENCE: Annals of the New York Academy of Sciences, 338:276-296, May 15, 1980.		
16. ABSTRACT The purpose of this study was to gather definitive scientific results about the formation and transport of ozone and fine aerosols. Such information would greatly aid in designing a rational control strategy for secondary pollution, based on the control of precursor emissions. The co-occurrence of elevated levels of ozone and light scattering aerosols, particularly sulfates, has been shown in regional scale episodes, in large urban plumes, in aging power plant plumes and in smog chambers. In this report, MISTT data from the Labadie power plant plume is re-examined to investigate the ozone-aerosol link more closely and to identify the ambient conditions most conducive to the generation of the smog-haze pollution. A variety of air quality as well as meteorological and navigational parameters were continuously measured from aircraft. Based on theoretical and empirical grounds, findings show a close link between the formation of ozone and aerosols in power plant plumes. The conditions of the back-ground air mass into which the plume is emitted and plume background interactions were found significant in the co-generation of ozone and aerosols during long range transport of power plant plumes. Ozone formation was found to be a significant factor. Total nitrate formation may well exceed aerosol sulfate formation during the first several hours of plume transport. This subject deserves more attention in future research.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

PR81-166621

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Reprinted from
ANNALS OF THE NEW YORK ACADEMY OF SCIENCES
Volume 338 Pages 276-296
May 15, 1980 27134

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SPRINGFIELD, VA 22161

FORMATION AND TRANSPORT OF OZONE AND AEROSOLS IN POWER PLANT PLUMES*

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INTRODUCTION

In industrial regions, it is common for ozone and light scattering aerosols to occur concurrently. Seasonally, both ozone and aerosol sulfate concentrations exhibit peaks in the summer months. Diurnally, the formation of both is maximum on warm sunny afternoons. In the eastern United States, the spatial distribution patterns of ozone and sulfates are also believed to have a similar regional character. The cooccurrence of elevated levels of ozone and light scattering aerosols, particularly sulfates, has been shown in regional scale episodes,¹ in large urban plumes,² in aging power plant plumes,³⁻⁵ and in smog chamber experiments.^{6,7}

The regional distribution of ozone and sulfates is now generally accepted as being due largely to the long range transport and transformations of the precursors (SO_2 , NO_x , hydrocarbons, etc.) emitted from large urban-industrial and power plant sources.^{8,9} Owing to the interaction of many plumes over large areas, and the complex nature of atmospheric transport and chemistry, the task of designing and implementing a rational control strategy for secondary pollution, based on the control of precursor emissions, is a most difficult one. Definitive scientific results about the formation and transport of ozone and fine aerosols (sulfates, nitrates, as well as organics) are needed.

White *et al.*² examined the formation of ozone and light scattering aerosols during the daytime transport of a well-defined urban plume of St. Louis out to nearly 200 km under particularly favorable transport conditions. In that analysis of aircraft measurements, it was observed that following an initial period (~1 hr) of limited activity, ozone and light scattering aerosols, particularly sulfates, were formed in the plume substantially in excess of the background levels. The main impact region was more than 50 km downwind of the source area. For various practical reasons, the plume was not sampled beyond 200 km. This range was exceeded in the flight of the DaVinci II balloon¹⁰ embedded in the St. Louis plume. The secondary pollution that formed in the plume during the afternoon was transported overnight in a layer decoupled from the ground. The elevated pollution of St. Louis was then entrained into the growing mixing layer of the next morning and brought down to ground in western Indiana.

*Supported by U.S. Environmental Protection Agency Grant No. R805918.

Gillani *et al.*⁴ and Gillani¹¹ described in quantitative detail the formation and transport of sulfates in the Labadie power plant plume over distances exceeding 300 km on two separate occasions (July 9 and 18, 1976; see FIGURE 1). Both times, plume transport was tracked through day and night, providing unique data that led to direct evidence and documentation of the dominant role of sunlight in the oxidation of SO_2 to sulfates in the atmosphere (FIGURE 2; upper). The maximum gas-to-particle conversion rate of sulfur was observed in the afternoon hours, when ozone formation also peaked to levels well in excess of the background. The dependence of sulfate formation

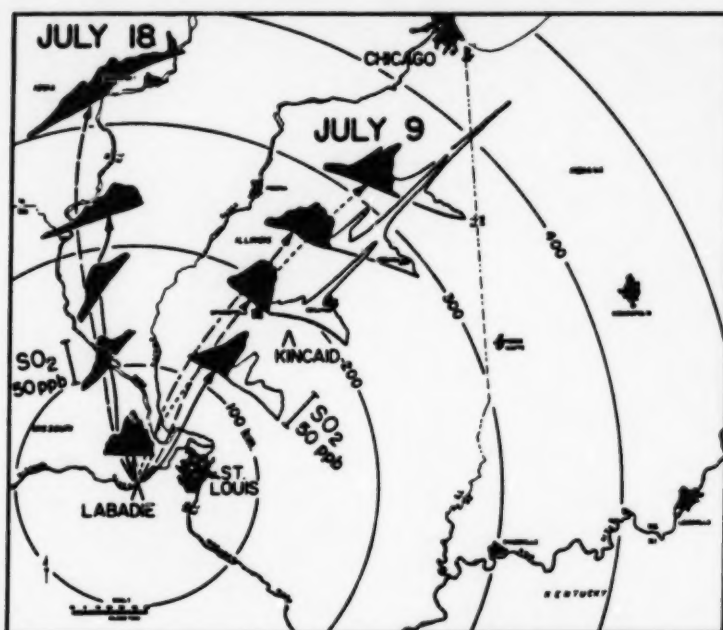


FIGURE 1. Crosswind plume profiles of SO_2 during selected constant-altitude aircraft traverses on July 9 and July 18, 1976. The Labadie power plant plume sections are shaded. Also shown are backward trajectories for the Labadie plume (from Reference 4).

rate on sunlight, while crucial, is not unique. On July 9 and 18, different amounts of particulate sulfur formed in the plume for the same sunlight dose. A number of factors other than sunlight, but driven by sunlight, could also influence sulfate formation rate. Chief among these factors are enhanced ambient and dew point temperatures, atmospheric mixing, convective cloud formation, and photochemistry. Consequently, the roles played by all these factors except clouds (no data available) were examined. The difference in sulfate formation rates for the two days could be explained by differences in mixing and photochemical activity (ozone formation). Mixing and ozone formation were significantly more intense on July 18, the day with the higher

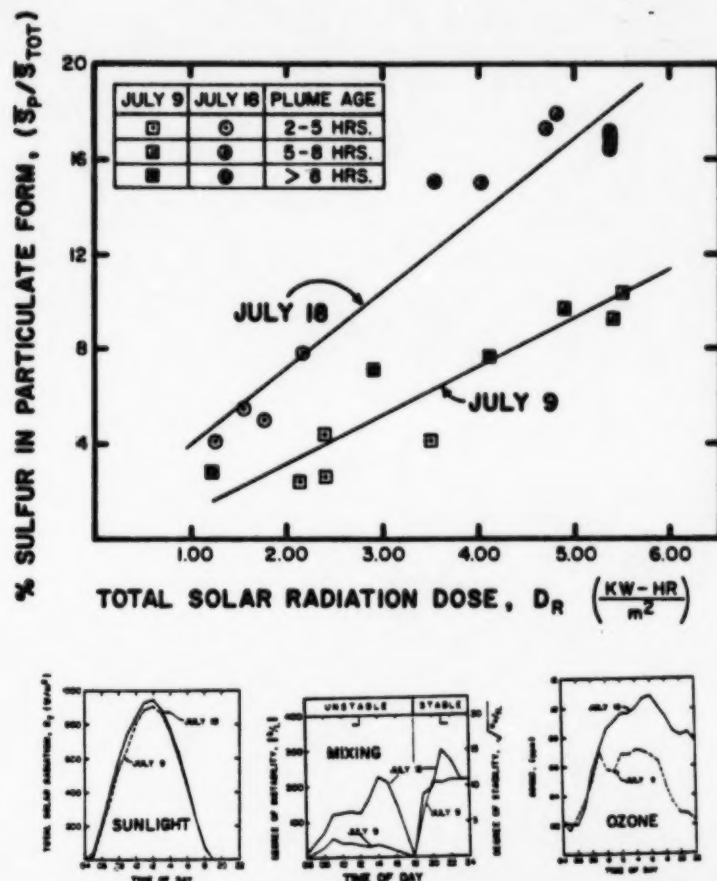


FIGURE 2. Upper: Ratio of particulate-to-total sulfur concentrations (average for traverse) as a function of total plume solar radiation dose, D_R (time integral of incoming solar radiation flux, R_T , between plume release time and plume sampling time). Lower: Comparisons of the temporal variations of incoming solar radiation flux, R_T , atmospheric stability parameter, and ozone concentrations for July 9 and 18, as measured at RAMS Station 118 (from Reference 4).

sulfate formation rate (FIGURE 2; lower). Based on the motivation provided by the above results, Husar *et al.*¹² examined the Labadie plume data of five more days and verified the diurnal variability of the sulfate formation rate. Then, using this observed diurnal pattern, they extrapolated the results and suggested that as much as 30-45% of the sulfur emissions from the power plant may ultimately be converted to sulfates. This process would take several days of plume transport ranging over a regional scale.

The urban and power plant plume data referred to in the above studies^{2,4,9,11,12} were all collected as part of Project MISTT, sponsored by the U.S. Environmental Protection Agency (EPA). In this paper, the MISTT data of the Labadie power plant plume are reexamined to investigate the ozone-aerosol link more closely, and also to identify the ambient conditions most conducive to the generation of the smog-haze pollution. Hopefully, such information will aid in designing control measures that properly reflect the role of interactions between anthropogenic emissions of the precursors and the ambient atmosphere. Preliminary observations in the data collected as part of EPA's Project STATE/Tennessee Plume Study (August 1978) appear to support the conclusions drawn in this paper.

EXPERIMENTAL

The results presented in this paper are based primarily on the MISTT data of Labadie plume transport on 9, 14, 18, and 30 July, 1976. The data were collected aboard the following two aircraft: Washington University (WU) AeroCommander (July 9, 18); Meteorology Research, Inc. (MRI) Cessna 206 (July 14, 18, 30). The aircraft were instrumented for continuous measurements of a variety of air quality (gaseous as well as aerosol), meteorological, and navigational parameters. Particulate sulfur measurements, however, were based on filter sample collections with subsequent laboratory analysis. Grab samples of the ambient air were also collected in the MRI aircraft and subsequently analyzed for hydrocarbon species. More detailed descriptions of the airborne platforms, instrumentation, and measurements are given in References 12 and 13. In the MISTT plume study, the standard aircraft sampling pattern included crosswind plume traverses and vertical spirals at different distances downwind of the source, supplemented by sampling in the background air.

For the analysis of the MISTT data, use is also made of the pertinent data of RAMS Station 118 (a rural station to the south of the metropolitan St. Louis area) of the Regional Air Pollution Study (RAPS), also sponsored concurrently by EPA.

The Labadie power plant of the Union Electric Company is located 60 km west of the Gateway Arch which is at the Mississippi riverfront in downtown St. Louis. It is a coal-fired, base-load plant with a rated capacity of 2400 MW. The plant has four boiler units feeding into three 214-m stacks. The monthly average sulfur content of the fuel in July 1976 was 3.17%. The sulfur emission rates for the four days of interest here ranged between 10 and 14 kg/s (as SO₂).

Labadie plume transport for July 9 and 18 is shown in FIGURE 1, and for July 14 and 30 is shown in FIGURE 3. The July 9 plume mixed into a warm, moist, and somewhat stable gulf air mass. Wind speeds ranged from 6–8 m/s in the morning, increased gradually in the afternoon, and reached 20 m/s by midnight. The July 18 air mass belonged to a slow circulation (afternoon wind speed, 3–4 m/s) around a continental high pressure cell to the east. Skies in the sampling area remained very clear, and visibility remained unrestricted throughout the day. On July 14 and 30, air mass trajectories were generally from Texas and Oklahoma. On July 14, the sampling area was in a wedge formed by a warm front to the east and a cold front to the west. Skies were generally clear, except for patchy fog in the morning. A semistationary front continued to oscillate in the sampling area through most of July 30. Skies were partly cloudy to cloudy during the sampling period.

APPROACH OF DATA ANALYSIS

A central hypothesis and conclusion of this paper is that the condition of the background air mass into which the plume is emitted and plume-background interactions are of paramount significance in the formation of both ozone and aerosols during the long range transport of power plant plumes. During the photochemically active daylight hours, chemical reactions between two species that are both of primary origin will become rapidly quenched¹⁴ as the plume dilutes. Thereafter, and for the entire subsequent plume transport, the primary plume species (e.g., SO_2 , NO_x) will

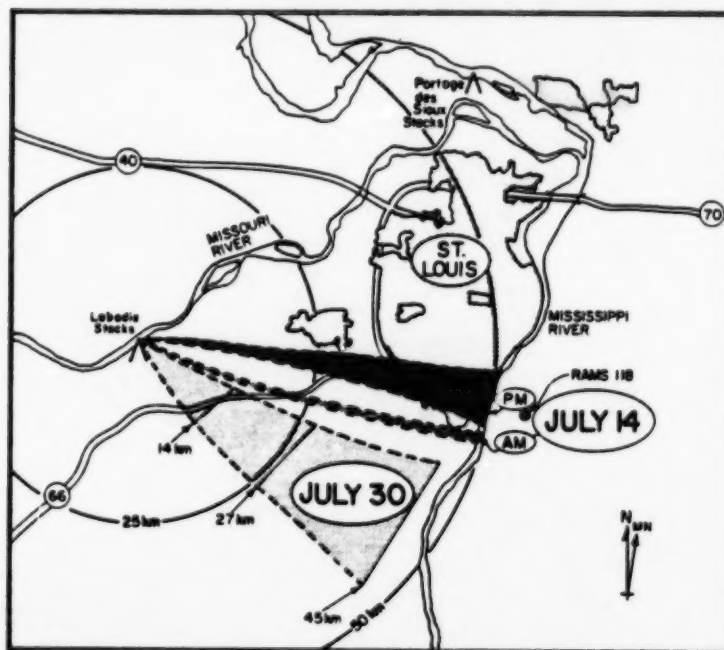


FIGURE 3. Labadie plume transport and aircraft sampling sections for July 14 and July 30, 1976.

react ever increasingly with reactants of background or secondary origin. The local ratio of background to plume air is a crucial parameter, governing the formation rate of ozone as well as aerosols. This ratio varies along the plume centerline for increasing distance of plume transport, as well as along crosswind plume traverses at a given plume cross section. In past studies, in general, integrals of crosswind plume data or integrals of cross-sectional plume data at increasing downwind distances have been compared to infer plume kinetics.^{24,11} This approach is hampered by two practical shortcomings with respect to investigation of plume-background interactions. Firstly, the maximum downwind range covered has been limited to 300 km under the most

favorable transport conditions. Hence, only a fraction of the full range between 100% plume air (at the source) and 100% background air (very far downwind) is covered. Secondly, the measurements are at discrete points of the spectrum because the aircraft measurements are not truly Lagrangian. In contrast, each crosswind plume traverse by the aircraft during the early hours of plume transport yields a continuous profile of almost the entire spectrum between nearly 100% plume air (at the core) and 100% background air (at plume edges).

An additional attractive feature of the crosswind plume data at early transport times is that they can be obtained in a single plume traverse by the aircraft within a few minutes. The data thus approximate a steady state "snapshot" of a plume section with respect to pollutant concentrations, while the effect of variable mixing is highlighted. The plume core approximates conditions of plume-to-background ratio that would exist in a stable, coherent plume, while the plume edges approximate conditions representative of a rapidly dispersing plume. In other words, the role of mixing in plume chemistry is isolated for study, while other factors remain in a steady state. Needless to say, the role of mixing in plume-background interactions is crucial. Plume-background interactions are probably especially important in power plant secondary pollution formation, because an essential ingredient (reactive hydrocarbons) for significant photochemical ozone-aerosol formation is missing in power plant primary emissions and must be entrained by mixing from the background air.

For the reasons stated above, the emphasis in this paper is on examination of crosswind plume profiles of primary, as well as secondary, species.

Our approach in data examination and presentation is motivated by one other hypothesis, which concerns the practical significance and utility of ozone in assessing aerosol formation rate. The chemistry that leads to aerosol formation in plumes is very complex. A very large number of chemical species have been identified as relevant reactants, and an even larger number of reactions have been postulated. Many of these species have never been measured in the atmosphere, and many of the reaction rates are either not known at all, or are known with little confidence. For practical simulations at the present time, therefore, it is necessary to resort to lumped parametrizations and empirical relations, based on a very limited number of species acting as surrogates for the many. The development of such parametrizations or empirical relations, to be used as submodels representing the chemical transformation terms in long range transport models, is one of the principal, and most pressing, goals of many current research programs. In this paper, data are presented that suggest a basis for the possible use of ozone as a surrogate for the radical species believed to be the principal agents for the oxidation of SO_2 and NO_2 in the gas phase. The theoretical and empirical bases for such use of ozone as a surrogate quantity are briefly examined. Finally, the conditions believed to be conducive to ozone generation in power plant plumes are identified and are shown to be also favorable to aerosol formation.

OZONE-AEROSOL LINK: THEORETICAL BASIS

Aerosol Formation

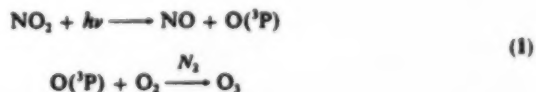
Sulfate, nitrate, and organic fine aerosols are formed from the precursor gases (SO_2 , NO_2 , HC, CO) in the atmosphere. The oxidation of SO_2 in the gas phase is

believed to occur principally by three key free radicals: $\text{OH}\cdot$, $\text{HO}_2\cdot$, and $\text{RO}_2\cdot$.^{13,16} If the atmosphere is "clean," i.e., hydrocarbon-poor, the role of $\text{OH}\cdot$ is predominant. $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ will become increasingly important as more reactive hydrocarbons become available.† In the liquid phase, O_3 and H_2O_2 may be the dominant oxidizing agents during long range plume transport.^{17,18} All five oxidizing species named above, viz., $\text{OH}\cdot$, $\text{HO}_2\cdot$, $\text{RO}_2\cdot$, O_3 , and H_2O_2 , are photochemically generated. Of the five, only O_3 has been measured extensively in the atmosphere. The difficulty in measuring the other species in the atmosphere is a significant hindrance to a full understanding of the mechanisms responsible for the conversion of SO_2 to sulfates. It is also for this reason that the validity of ozone as a reasonable surrogate for the radical species would be a substantial advantage.

The oxidation of NO_2 by $\text{OH}\cdot$ or O_3 and of NO by $\text{HO}_2\cdot$ can lead to the formation of HNO_3 .¹⁹ HNO_3 has a high vapor pressure at ambient temperatures and cannot exist as aerosol except in the presence of water or sulfuric acid droplets.¹⁹ The formation of particulate nitrate may result from gas phase reactions of HNO_3 with NH_3 or from liquid phase oxidation of dissolved NO_2 .

Ozone Formation

The only proven chemical source of O_3 in the troposphere is the photolysis of NO_2 :



Its principal sink in the plume is the reaction with NO :



In a fresh plume, ambient ozone is rapidly depleted by reaction with NO , leading to the well-known ozone deficit. During the daytime, a gradual recovery of ozone will occur as NO_2 is produced, and a photostationary state is rapidly reached in which the concentration of ozone is directly proportional to the NO_2/NO concentration ratio. No net production of ozone can take place in this photolytic cycle in the absence of competing reactions.

In several recent studies, a net generation of ozone in excess of the background level has been observed in power plant plumes.^{3-5,20,21} This can occur under certain conditions when the ozone source reaction (1) continues while ozone depletion (Reaction 2) is slowed down by the following competing reactions involving the peroxy radicals $\text{RO}_2\cdot$ and $\text{HO}_2\cdot$:

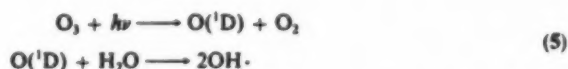


†Very recent laboratory studies^{22,27} have suggested that the role of $\text{HO}_2\cdot$ in the direct oxidation of SO_2 , as well as in the breakdown of hydrocarbons and the subsequent formation of ozone, is of relatively negligible significance compared to the role of $\text{OH}\cdot$.

In other words, these peroxy radicals participate in the oxidation of SO_2 as well as in the generation of excess plume ozone.[†] This is the first important link between ozone and sulfate formation in plumes. A second link concerns the source of the peroxy radicals. Both $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ are formed during the consumption of reactive hydrocarbons entrained into the plume from the background air by mixing. During the early hours of plume irradiation, $\text{OH}\cdot$ is by far the most important agent that attacks the hydrocarbons to generate $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$.¹⁹ Thus, the hydroxyl radical ($\text{OH}\cdot$), which plays an important role in the formation of sulfates, is also a key participant in the generation of ozone in the plume.

The free radical link between ozone and aerosol generation in the power plant plume thus depends on plume NO_x , hydrocarbons in the background air, and sufficient mixing to entrain the hydrocarbons into the plume. Thus, the ratio of background-to-plume air is related to the ratio NMHC/NO_x ,[‡] which has been shown in smog chamber studies to be a strong factor in the homogeneous oxidation of SO_2 .²²

If the plume transport is in a "clean" atmosphere, the ozone-aerosol link is more direct. In this case, $\text{OH}\cdot$ is the predominant agent for oxidizing SO_2 , and O_3 is its principal source:



In a clean background, however, ozone generation and recovery in the plume will be limited, and the overall rate of sulfate formation will also be expected to be slower than for the case of plume transport in a polluted air mass.

In summary, the radicals $\text{OH}\cdot$ and $\text{RO}\cdot$ are the common link between the generation of ozone and of aerosols in the power plant plume when the following conditions are met: precursors SO_2 , NO_x in the plume; precursor hydrocarbons in the background; mixing, to entrain the hydrocarbons into the plume; and sunlight, to drive the photochemical processes.

OZONE-AEROSOL LINK—PLUME OBSERVATIONS

During the summer, ozone and aerosol formation in plumes is most intense after the first hour or so of plume transport during the afternoon. In the July 1976 field program of Project MISTT, aircraft sampling was performed in a clearly identifiable Labadie plume for two or more hours of afternoon transport on six separate days—July 5, 9, 12, 14, 18, and 30. On all six afternoons, ozone generation in excess of the background level was realized. In this paper, the data of July 9, 14, 18, and 30 are selected for presentation because, between them, they include the extreme conditions and, together, they provide data that are representative of the summer conditions in the Midwest.

[†]Very recent laboratory studies^{23,27} have suggested that the role of $\text{HO}_2\cdot$ in the direct oxidation of SO_2 , as well as in the breakdown of hydrocarbons and the subsequent formation of ozone, is of relatively negligible significance compared to the role of $\text{OH}\cdot$.

[‡]NMHC = nonmethane hydrocarbon.

TABLE I
SUMMARY OF AIRCRAFT SAMPLING, AMBIENT AIR QUALITY, AND SULFUR
GAS-TO-PARTICLE CONVERSION RATES (R_{s-s_2}) IN THE LABADIE
POWER PLANT PLUME (JULY 1976)

Date	Downwind Distance (km)	Approximate Sampling Time	Plume Age (hr)	Background Levels			$R_{s-s_2}^*$ (% hr ⁻¹)
				b_{sm} (10 ⁻⁴ m ⁻¹)	TNMHC† (μg/m ³)	Ozone (ppb)	
July 9 (WU)	70‡	1045-1200	3.0	2.1	NA	60	0.8
	105	1230-1245	4.5	2.0	NA	60	0.9
	135	1530-1630	6.5	1.7	NA	60	1.6
	190	2000-2100	8.5	1.5	NA	60	0.9
	250	2130-2200	9.8	1.5	NA	55	0.7
	310	2345-0015	9.2	1.6	NA	55	0.3
July 14 (MRI)	47	0720-0745	1.3	1.0	147	65	0.1
	50	0800-0830	1.4	1.0	NA	65	0.3
	50	1200-1300	2.8	1.0	229	70	0.8
July 18 (WU)	30	1420-1530§	2.2	0.6	148†	100	3.2
	110	1540-1620	6.0	0.5	NA	100	3.0
	160	1815-1930	8.5	0.5	NA	85	2.0
	220	1945-2015	10.0	0.5	NA	80	1.6
	320	2345-0015	12.0	0.5	NA	70	1.2
July 30 (MRI)	14	1150-1215	1.0	1.3	164	75	1.0
	27	1230-1310	2.5	1.3	159	78	1.3
	45	1405-1420	4.2	1.3	NA	78	3.0

*Average conversion rate between plume release time and plume sampling time.

†Total nonmethane hydrocarbons (light + heavy hydrocarbon species). Samples collected in MRI aircraft.

‡(x) = first observation of ozone bulge in Labadie plume core at x km from source.

§WU and MRI.

†Not including light hydrocarbons.

On July 9 and 18, sampling was done over a long range (FIGURE 1), while on July 14 and 30, sampling was over a short range (FIGURE 3). TABLE I summarizes the sampling times and locations, the ambient air quality, and the sulfur gas-to-particle conversion rates for all four days. Gas-to-particle conversion of sulfur and the ozone bulge formation are taken as indices of secondary pollutant formation in the plume, while the ambient ozone level is interpreted as an index of the potential for photochemical smog formation in the background. The sulfur conversion rates on all four days peaked in the afternoon, the nighttime and early morning rates being the lowest. Of the four days, July 18 and 30 were the higher conversion days (peak $R_{s-s_2} \geq 3\% \text{ hr}^{-1}$), while July 9 and 14 were relatively lower conversion days (peak $R_{s-s_2} \leq 1.6\% \text{ hr}^{-1}$). Ambient ozone was significantly higher on the days of higher plume sulfur conversion. Since the peak conversion rates are averaged over transport times varying from 2.2 hr (July 18) to 6.5 hr (July 9), such a comparison of the rates can be misleading. Consequently, plume conditions are compared at the times when an ozone bulge is first observed over the entire plume. The downwind distance where such a condition is first observed on each day is circled in TABLE I.

Plume and ambient data at the first observation of the ozone bulge are isolated in TABLE 2. On all four days, plume ozone exceeded background ozone over an entire crosswind traverse for the first time within 2 to 3 hours of transport. The earliest time of observation of an ozone bulge was about noon. On July 18 and 30, the bulge appeared within 30 km of the source, while on July 9 and 14, 50 km or more of transport was required. In terms of sulfur conversion rate, July 18 stands out with a value of $3.2\% \text{ hr}^{-1}$, July 30 comes in a distant second at $1.3\% \text{ hr}^{-1}$, and July 9 and 14 trail last with $0.8\% \text{ hr}^{-1}$. The background ozone values show a similar ranking. Data of the transport of the Milwaukee urban plume over Lake Michigan for two summer days also showed a similar behavior, with R_{SO_2} being $4\text{--}11\% \text{ hr}^{-1}$ and $<1\% \text{ hr}^{-1}$, respectively, corresponding to background ozone levels of 95 ppb and $<50 \text{ ppb}$.²³ Evidently, plume sulfate formation relates well to the photochemical smog formation potential of the background.

Conditions Conducive to Ozone and Sulfate Formation

The principal measured parameters likely to influence ozone and aerosol formation during long range transport of the Labadie plume under midwestern summer conditions are believed to be the following:

Primary emissions: SO_2 , NO_x ;

Background: nonmethane hydrocarbons, ozone, b_{aerosol} ;

Meteorological: sunlight, low-level clouds (no quantitative data), temperature, relative humidity (RH), and mixing.

Of these quantities, the emissions of SO_2 and NO_x were only slightly variable for the four days. However, it has previously been reported that ozone bulges are more likely to form in the plumes of intermediate-size power plants, compared to plumes of large power plants with higher NO_x emissions.²⁰ The significance of the meteorological and background parameters is assessed below.

FIGURE 4 shows the hourly data of incoming solar radiation, temperature, and relative humidity, measured at the rural, ground-level Station 118 of the RAMS network of the St. Louis Regional Air Pollution Study. Superimposed on each daily trace of each parameter is a heavy solid line, covering the transport period from plume release to the time of first observation of the ozone bulge (see TABLE 2).

The solar radiation pattern is nearly the same for all days except July 30, when

TABLE 2
AMBIENT CONDITIONS AND R_{SO_2} AT FIRST OBSERVATION OF OZONE BULGE IN THE
LABADIE PLUME CORE (JULY 1976)

Date	Downwind Distance (km)	Approximate Transport Period	Plume Age (hr)	Background Levels			
				b_{aerosol} (10^{-4} m^{-1})	TNMHC ($\mu\text{g}/\text{m}^3$)	Ozone (ppb)	R_{SO_2} ($\% \text{ hr}^{-1}$)
July 9	70	0850–1150	3.0	2.1	NA	60	0.8
July 14	50	0900–1150	2.8	1.0	229	70	0.8
July 18	30	1350–1600	2.2	0.6	148*	100	3.2
July 30	27	1000–1230	2.5	1.3	159	78	1.3

*Not including light hydrocarbons.

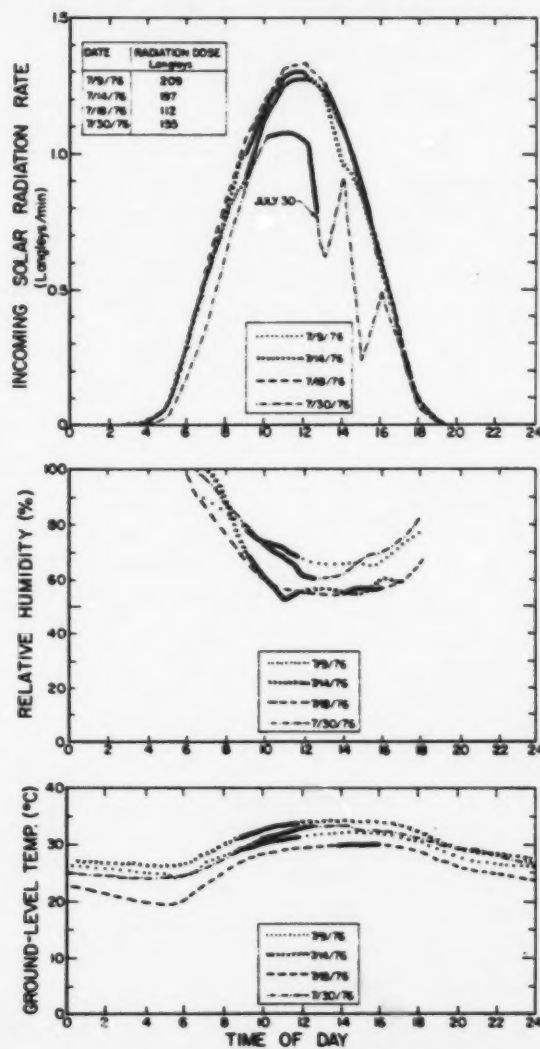


FIGURE 4. Comparison of solar radiation flux, ambient temperature, and relative humidity for July 9, 14, 18, and 30, 1976, as measured at RAMS Station 118. The heavy solid line on each trace emphasizes the conditions between plume release and the first observation of the ozone bulge in the Labadie plume.

the skies become progressively more cloudy during the day. The other days had more or less clear skies (FIGURE 4). There was, nevertheless, sufficient total plume exposure to sunlight (155 Ly) on July 30 to result in the formation of an ozone bulge in at least one of five plume traverses at 27 km. Approximately the same Lagrangian plume parcel was sampled at 27 km and again at 45 km. The sulfur conversion rate between these two sampled distances exceeded $3\% \text{ hr}^{-1}$ between about 1230 and 1400. The participation of clouds in sulfate formation during these hours on July 30 is likely. As will be shown later, however, substantial photochemical activity was quite evidently also taking place during these hours. The data of July 18 show that a sunlight dose as low as 112 Ly is sufficient for an ozone bulge to form, if other conditions are particularly favorable.

Temperatures were high (28–34°C) on all four days during the afternoon hours of sampling (FIGURE 4). While no clear positive correlation between sulfate formation rate and temperature is evident (the lowest afternoon temperature of 28°C was recorded at Station 118 on the day with the highest measured sulfate formation rate, July 18), it is also evident that ozone bulge formation is favored on hot days with ground-level temperatures exceeding 28°C. The same observation was also made by Keifer.²⁰

Relative humidity (RH) ranged between 57% and 70% at Station 118 during the early plume transport periods leading to the ozone bulge formation (FIGURE 4). On July 5, for which plume data are not presented here, ground-level RH was as low as 49% in the afternoon while plume ozone bulge was evidenced in the aircraft data. As with temperature, no clear positive correlation is observed between ozone-aerosol formation rate and RH.

Of the meteorological parameters, *atmospheric mixing* appears to show the most direct and strong positive correlation with ozone and sulfate formation rates in the plume. In FIGURE 5, the intensity of mixing in the horizontal is compared for the four days in terms of horizontal plume spread, and mixing height is taken as a measure of vertical mixing (see inset). The crosswind plume profiles shown are for SO_2 distribution at the altitude where the peak SO_2 concentration was observed in the plume section where the ozone bulge was first observed. Horizontal as well as vertical mixing was strongest by a wide margin on July 18 (the day of most rapid ozone and sulfate formation in the plume), followed by July 30, and finally July 9 and 14.

Mixing is presumably so important because it dilutes plume NO_x , increases plume NMHC by entrainment from the background, and thereby causes a gradual increase in the ratio NMHC/NO_x , which controls ozone and aerosol formation under warm, sunny conditions. A wide variety of hydrocarbon species of varying reactivity are present in the atmosphere. An attempt was made in the hydrocarbon analysis (performed at Washington State University) to identify as many individual species as possible. Unfortunately, the bulk of the NMHC concentration was due to species not individually identified. The total NMHC concentrations for the four days (see Table 2) show no clear positive correlation with the rates of ozone and aerosol generation in the plume. Both in Project MISTT, 1976, and in the Tennessee Plume Study of Project STATE, 1978, ozone bulges appeared on nearly every afternoon of plume sampling. Presumably, both in the Missouri-Illinois area and in the Kentucky-Tennessee area, the lower atmosphere contains sufficient reactive hydrocarbons on

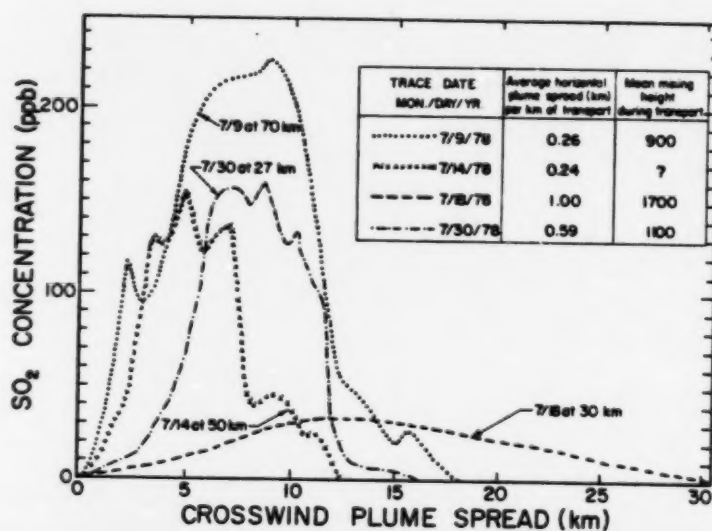


FIGURE 5. Comparison of mixing intensity for Labadie plume transport on July 9, 14, 18, 30. Crosswind profiles of SO_2 through the traverse closest to plume centerline in the cross section where ozone bulge was first observed. Inset: Comparison of horizontal and vertical mixing parameters.

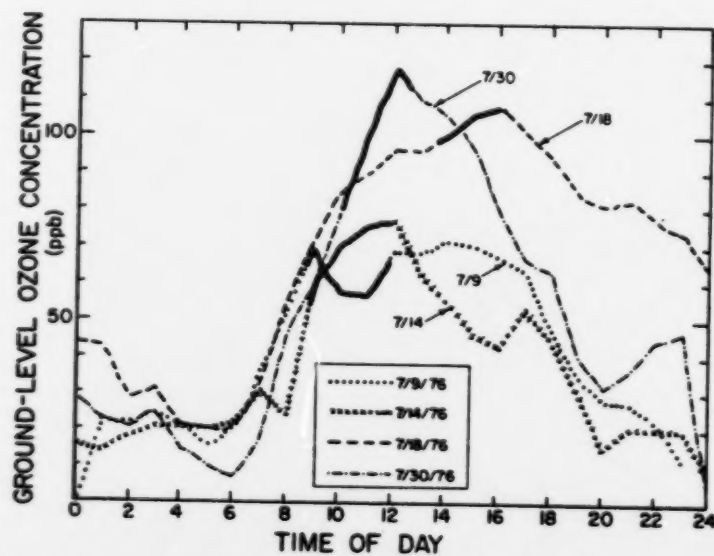


FIGURE 6. Comparison of the temporal variations of ozone for July 9, 14, 18, and 30, 1976, as measured at RAMS Station 118.

summer afternoons to permit ozone bulges to occur with far greater regularity than was previously believed.

The background ozone levels listed in TABLES 1 and 2 are based on aircraft data. The hourly ground-level ozone data at the rural Station 118 are shown for the four days in FIGURE 6. For the well-mixed conditions of the afternoon hours, ground-level data represent the conditions aloft reasonably well. Both the ground and the air data show clearly that high background ozone levels correspond to rapid secondary pollutant generation (July 18, 30) in the plume.

The background b_{max} values (TABLE 2) for the four days do not show a strong

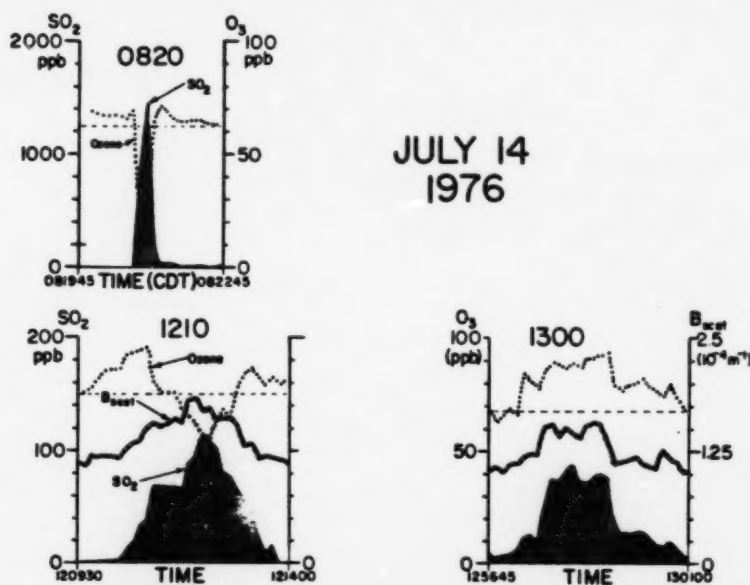


FIGURE 7. Crosswind plume data for 610 m MSL traverses at 50 km radial distance from Labadie at three different times on July 14, 1976. The three stages of secondary pollution formation are illustrated.

positive correlation with sulfate formation rate in the plume. None of the days, however, was particularly hazy. The air mass of July 18 (highest sulfur conversion rate) was the least hazy ($b_{\text{max}} = 0.6 \times 10^{-4} \text{ m}^{-1}$) but also had the highest background ozone. It was also the only one associated with a continental high pressure cell.

Stages in the Formation of Ozone and Aerosols

Three distinct chronological stages may be identified in the formation of ozone and aerosols during power plant plume transport in daylight. These three stages are illustrated in FIGURE 7, which shows crosswind plume profiles of SO_2 , O_3 , and b_{max} .

obtained during aircraft traverses made in the Labadie plume on July 14. All three traverses were made at about the same location, 50 km from the source (see FIGURE 3), at the same altitude (610 m MSL), but at different times of the day. The first traverse at 0820 represents the "early" stage (plume age is 1.4 hr), in which the primary emissions are concentrated in a narrow, coherent plume within which ozone is largely depleted as a result of its reaction with NO to form NO₂. There is little other interaction between the plume and the background, and R_{s-s} is low (0.3% hr⁻¹). The traverse at 1210 belongs to an "intermediate" stage, characterized by ozone bulges at the fringes of the plume resulting from strong interactions there between plume NO_x and the reactive hydrocarbons from the background. The ratio NMHC/NO_x is logically highest at the fringes. In the transition from the early to the intermediate stage, ozone deficit in the core of the plume is gradually recovered, more or less in keeping with the photostationary state cycle involving NO, NO₂, and O₃. The traverse at 1300 is the "fully developed" stage (plume age is 2.8 hr), in which background species have diffused through to the plume core and the ozone bulge has formed over the entire profile. The transitory early and intermediate stages have given way to a fully developed plume profile, which would persist as long as photochemistry could proceed. The distributions of the radical species linking ozone and aerosol formation have presumably reached steady state, evidenced by the high degree of correlation now existing between the ozone and b_{max} profiles. The average value of R_{s-s} is now 0.8% hr⁻¹.

The three stages are once again illustrated in the data of July 30 (FIGURE 8). Here,

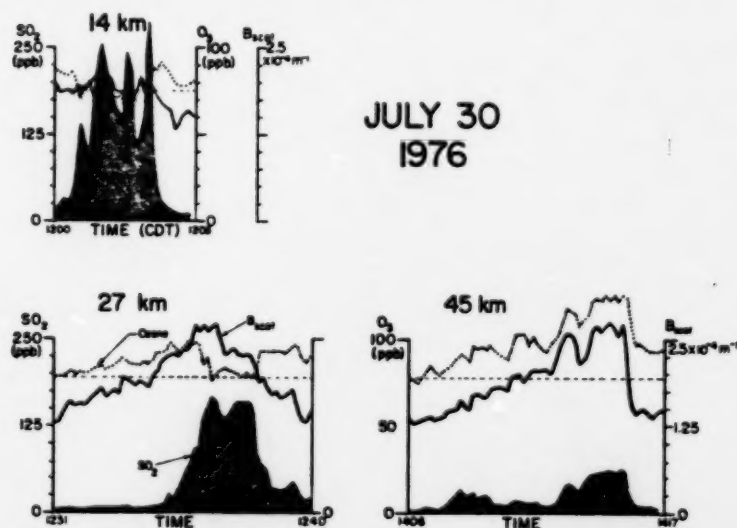


FIGURE 8. Crosswind plume data for traverses at 14, 27, and 45 km radial distances for Labadie on July 30, 1976. The "early," "intermediate," and "fully developed" stages of secondary pollution formation are illustrated. Observe, in particular, the fringe enhancement of secondary pollution parameters relative to SO₂ in the data at 27 km.

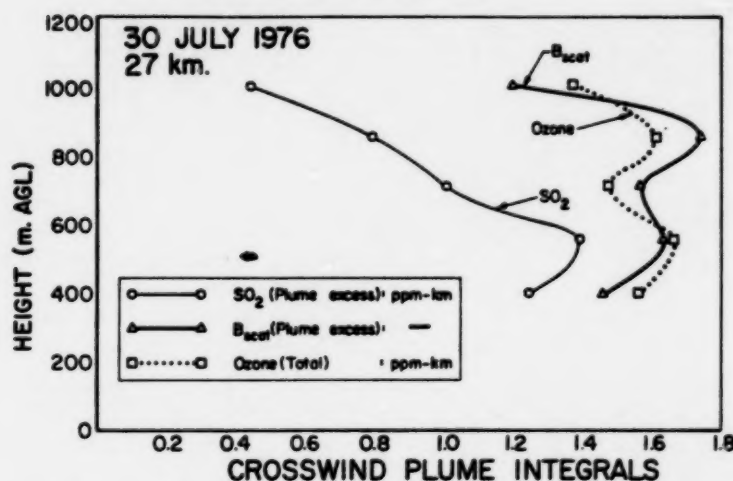


FIGURE 9. Vertical profiles of the Labadie plume of July 30, 1976 at 27 km. Each data point represents the crosswind plume integral of the parameter over a given traverse trajectory. Observe the enhancement of the secondary pollution parameters at the upper edge of the SO_2 plume.

quasi-Lagrangian plume profiles are shown at 14 km, 27 km, and 45 km radial distances from the source and correspond to plume ages of about 1, 2.5, and 4.2 hours, respectively. An important consequence of plume-background interactions is illustrated in the plot of the intermediate stage at 27 km. The ozone bulges at the fringes indicate the generation of the peroxy radicals there, which causes a higher rate of aerosol formation there than at plume core. The $b_{\text{aer}}/\text{SO}_2$ ratio is thus higher at the fringes, and the aerosol plume has the appearance of being substantially broader than the SO_2 plume. The same fringe effect is obtained also in the vertical plume profiles at the intermediate stage, shown in FIGURE 9. Observe that the highest value of the ratio $b_{\text{aer}}/\text{SO}_2$ is near plume top, where SO_2 is low. The conversion rate of sulfur increases from 1.0 to 1.3 to 3.0% hr^{-1} as the plume develops through the three stages. Similar stages in the development of the power plant plume have also been observed by Davis *et al.*²⁴

Two striking illustrations of fringe-enhanced aerosol formation by homogeneous gas phase mechanisms are shown in FIGURE 10. Observe the "spikes" of the Aitken Nuclei Count (ANC) near plume edges. Fringe enhancement of aerosol production also has been investigated recently by White.²⁵

The time it takes for the plume to develop to the mature third stage depends largely on the availability of the reactive hydrocarbons in the background and the intensity of mixing. Under summer daytime conditions, this process would take a few hours. Thereafter, the mature conditions would persist until the sunlight level became insufficient to drive the photochemistry. A question of obvious importance for long range plume transport is: What happens to an aged plume after a hard day's journey into the night?

The Labadie plume transport was sampled during the day and night on July 9 (see FIGURE 1 and TABLE 1). Crosswind plume profiles at 70 km (ca. 1100), 135 km (ca. 1600), 190 km (ca. 2000), and 310 km (ca. midnight) are shown in FIGURE 11. The profile at 70 km is in the intermediate stage. The developed profiles at 135 km and 190

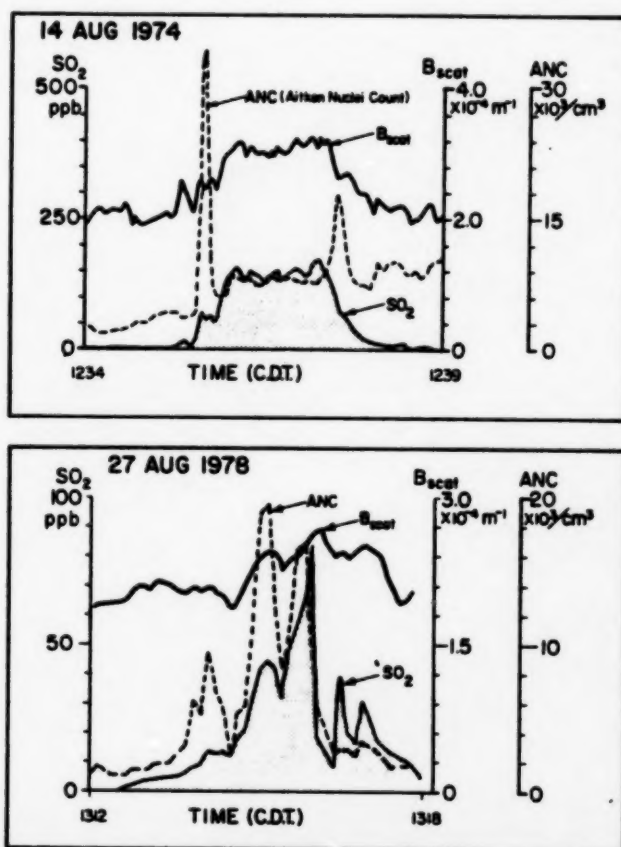


FIGURE 10. Examples of enhanced homogeneous nucleation (Aitken Nuclei Count) at plume fringes for the Labadie plume of 8/14/1974 (upper) and the Cumberland plume of 8/27/1978 (lower).

km are at different ages. The 190 km and 310 km profiles, though not belonging to the same plume parcel, illustrate what happens to an aged daytime plume during the night. There is no new generation of ozone or of the photochemical radical species at night. Plume NO level is also largely depleted following many hours of daytime

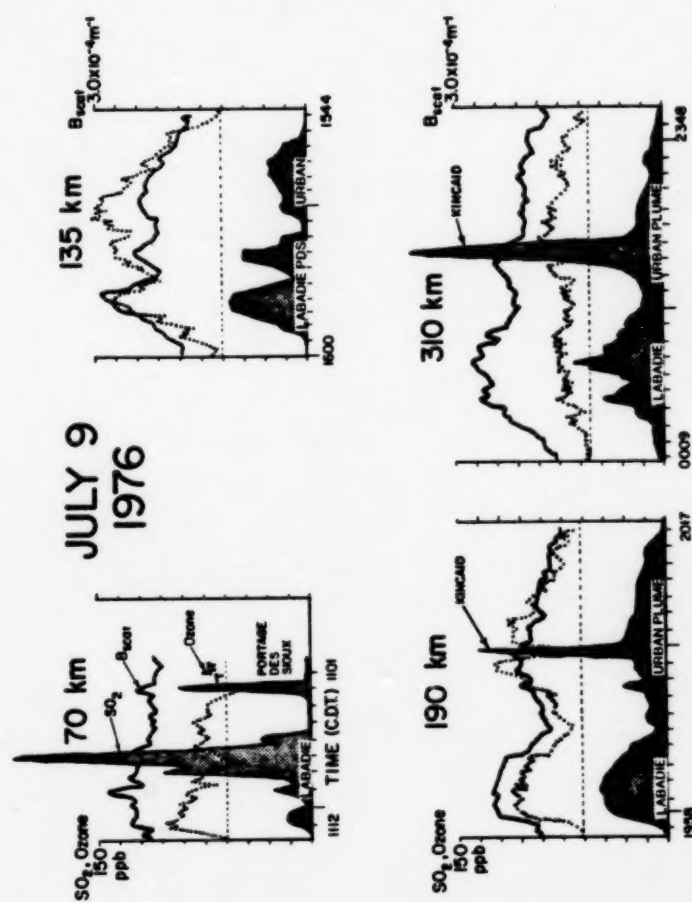


FIGURE 11. Crosswind plume data of the St. Louis plumes of July 9, 1976 at 70, 135, 190, and 310 km radial distances from the Labadie stacks. Daytime generation of secondary pollution, and its dispersion by shear at night.

transport. Consequently, ozone depletion is also slow, if any. One would expect logically, therefore, that the plume ozone bulge would be maintained and transported overnight. By midnight on July 9, however, the ozone bulge of the afternoon had diminished and broadened substantially. The most likely explanation, we suggest, is the wind shear effect. During the night, a considerable directional shear in the wind caused the plume to spread out over a large volume, and led to the termination of the mission. In the absence of strong wind shear, the secondary formations could be expected to carry over into the next day largely intact.

Oxidation of NO₂

No data were collected of HNO₃ or particulate nitrate concentrations in Project MISTT. However, based on the NO₂ data and the reaction kinetics of NO₂ oxidation, a substantial amount of HNO₃ formation may be expected to occur. NO₂ oxidation occurs primarily by OH· and O₃. The oxidation of NO₂ by OH· is more than an order of magnitude faster than the oxidation of SO₂ by OH·.¹⁶ Consequently, whenever the ratio NO₂/SO₂ exceeds 0.1 in the plume, nitric acid formation may exceed sulfate formation. In the Labadie plume of July 30, the NO₂/SO₂ ratio increased from an average 0.18 at 14 km, to 0.22 at 27 km, and 0.33 at 45 km. In the first four hours of daytime plume transport, nitric acid formation not only may have exceeded sulfate formation, but may have done so increasingly with plume transport. This dominance could have persisted for much longer times. If sufficient NH₃ is available from the background, significant formation of particulate nitrates may also result. These data serve to point out the need for more measurements and investigation of this subject.

SUMMARY AND CONCLUSIONS

A case is made, based on theoretical and empirical grounds, that a close link exists between the formation of ozone and aerosols in power plant plumes. The condition of the background air mass (NMHC loading), the extent of plume-background interactions, and photochemical processes are suggested as factors of paramount importance in the cogeneration of ozone and aerosols in plumes on warm summer days in the U.S. Midwest. The ambient ozone level is a good indicator of background reactivity. Ambient ozone and mixing are the major easily measurable factors that relate to the NMHC/NO_x ratio in the plume and, hence, to the rates of generation of secondary pollutants. A moderate amount of sunlight exposure (~110 Langley), ground-level temperature above 28°C, and relative humidity above 50% are sufficient conditions for rapid formation of excess plume ozone and aerosols. Ozone bulges appear in power plant plumes on warm summer afternoons quite regularly in the Midwest.

The radical species OH· and RO₂· are possibly the principal intermediates in the ozone-aerosol link. The role of OH· is dominant in the early stages of plume transport and during transport in a relatively clean background. RO₂· gains in importance with increasing plume transport and with increasing amount of reactive hydrocarbons in the background. So does ozone. The practical significance of ozone—not only in its

own right, but also in the formation and long range transport of aerosols—is potentially great. Until the important radical species are easily measured in the atmosphere, ozone may serve as a good surrogate for them in the development of empirical parametrization of the submodule for chemical transformations in long range transport models for aerosols.

Based on the plume data of Project MISTT, three distinct stages of daytime plume development are identified. An early stage is dominated by the primary emissions and an ozone deficit. An intermediate stage is dominated by enhanced formation of ozone and aerosols in plume fringes as the early manifestation of entrainment of background species into the plume. Ultimately, a quasi-steady, fully developed stage is attained, in which the entire plume has matching levels of the background species. As the stages develop, secondary pollution formation rate in the plume also increases rapidly. In the mature stage, secondary pollution dominates in the plume as it gradually advances to contribute to the regional scale background. Except under strong wind shear, the secondary pollutants may jet through the night, unabated in concentration.

Total nitrate formation may well exceed aerosol sulfate formation during the first several hours of plume transport. This subject deserves much more attention in the future.

ACKNOWLEDGMENTS

We thank participants of Project MISTT. The data from the Regional Air Pollution Study were provided to us by U.S. EPA, for which we are grateful. The drawings were made by David Chisholm.

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